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Effect of Metal Ion Addition in a Ni Supported Ga_2O_3 Photocatalyst on the Photocatalytic Overall Splitting of H_2O

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Abstract The effects of the addition of a metal ion in a Ni supported Ga_2O_3 photocatalyst on the photocatalytic overall splitting of H_2O were investigated. The addition of Ca, Cr, Zn, Sr, Ba and Ta ions were effective in improving the photocatalytic activity. Particularly, the addition of the Zn ion improved the photocatalytic activity remarkably. The states of the photocatalyst after the addition of Zn ion are discussed.

Keywords Photocatalytic overall splitting of H_2O · Ni supported Ga_2O_3 · Metal ion doping · Zn ion

1 Introduction

Photocatalytic overall splitting of H_2O is one of the important photocatalytic reactions. However, only a limited number of photocatalysts have been reported that are able to catalyse this reaction effectively [1, 2]. Recently, the series of oxides and mixed oxides of P-block elements with d^{10} electron configurations, such as the oxides containing Ga [3, 4], Ge [5], In [6–8], Sn [9], and Sb [10], have been reported to be photocatalytically active for the H_2O splitting reaction. Among them, Ni loaded Ga_2O_3 is one of the promising photocatalysts and shows relatively high photocatalytic performance in the H_2O splitting reaction. However, the performance of the photocatalyst is lower in comparison with photocatalysts of Ta based mixed oxides.

To improve the photocatalytic performance, various modifications, such as metal ion addition, have been carried out [11–13]. In particular, the photocatalytic activity of H_2O splitting was remarkably improved by the addition of La^{3+} ion to a $NaTaO_3$ photocatalyst [11, 12]. The particle size of $NaTaO_3$ became smaller and a nano-step structure appeared on the surface after the addition of La^{3+}. These morphological changes strongly influenced the improvement in efficiency of the photocatalytic H_2O splitting.

In this paper, we investigate the improvement of photocatalytic performance of Ga_2O_3. Here we report the influence of the addition of metal ions to the Ga_2O_3 photocatalyst on the photocatalytic performance of overall splitting of H_2O.

2 Experimental

The Ga_2O_3 photocatalyst used in the present work was obtained from High purity Chemical. The addition of metal ions was carried out by the impregnation method to the Ga_2O_3 from the aqueous solution which contained the prescribed amount of corresponding metal ion. The obtained precursors were calcined at prescribed temperatures in air.

Ni was used as co-catalyst for the H_2O splitting reaction. The loading of Ni co-catalyst was carried out by the photodeposition method. The prescribed amount of $Ni(NO_3)_2$ was dissolved in reactant H_2O. The deposition of Ni co-catalyst on Ga_2O_3 proceeded in the initial stages of the photocatalytic reaction. We have confirmed that preferable amount of Ni co-catalyst loaded over a Ga_2O_3 photocatalyst for H_2O splitting by this method was 1 wt%.

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Therefore, the photocatalysts loaded with 1 wt% of Ni co-catalyst were used in this study.

Photocatalytic reaction was carried out in an inner irradiation type photoreaction vessel made of quartz. The vessel was connected to the closed gas circulation system, with a volume of 500 ml, equipped with vacuum line and gaschromatograph sample inlet. The photocatalyst (1 g) was suspended in well out-gassed Ni ion containing deionized H_2O in the vessel and the irradiation from high pressure mercury lamp (450 W USHIO) started. The evolved gases were collected in the sampling tube in the system and analyzed by on line gaschromatograph (Shimadzu GC-8A).

The characterization of the photocatalysts was carried out by UV diffuse reflectance spectroscopy, XRD (Rigaku Rint-2200), and FE-SEM (Hitachi S-4800).

3 Results and Discussion

Figure 1 shows photocatalytic evolution of H_2 and O_2 in time over (a) Ni(1 wt%)/Ga_2O_3 and (b) Ni(1 wt%)/Zn (1 atom%)-Ga_2O_3. The Zn-containing Ga_2O_3 was prepared by calcining the precursor of Zn ion impregnated Ga_2O_3 precursor at 1,273 K for 10 h. As shown in Fig. 1a, H_2 and O_2 are produced at a constant rate after the induction period for 3 hours. In the induction period, O_2 was selectively produced due to the deposition of Ni co-catalyst on the Ga_2O_3 photocatalyst as shown in our previous report[3]. After the induction period for 1 h, as shown in Fig. 1b, H_2O decomposes stoichiometrically and it is clear that the rate of the splitting of H_2O is remarkably accelerated over the Zn ion modified Ga_2O_3. These results clearly show that the photocatalytic activity of Ga_2O_3 to H_2O splitting improved by the addition of Zn ion. The results in Fig. 1 also demonstrate that the addition of metal ion is one of the effective methods to improve the photocatalytic performance of Ga_2O_3 to the overall H_2O splitting. Therefore, the photocatalytic performance after the addition of other metal ions to Ga_2O_3 was examined.

The photocatalytic activities of various metal ion added Ga_2O_3 to the overall splitting of H_2O are listed in Table 1. The amount of added metal ion in Ga_2O_3 was 2 atom % and the photocatalysts were prepared by the calcination at 1,273 K. The photocatalytic activity in Table 1 is that of metal ion added Ga_2O_3 supported with 1 wt% of Ni co-catalyst, and was evaluated by the amount of produced H_2 and O_2 under the steady state of the photocatalytic overall splitting of H_2O for 1 h. From the results in Table 1, the additives can be separated into three groups on the basis of the influence on the photocatalytic activity. The additives, Ca, Sr, Ba, Cr, Ta, and Zn ions are belonging to the first group. As shown in Table 1, the photocatalytic activity of Ga_2O_3 improves on addition of ions belonging to the first group. Particularly, the photocatalytic activity of Zn ion modified Ga_2O_3 improves markedly. The additives, Mg, Ni and La ions are the second group. These additives do not influence to the photocatalytic activity very much compared to the non-modified Ga_2O_3 photocatalyst. The additives, Ti, Fe, Co, Cu, Nb, and Rh ions are a third group. These additives probably become a recombination center of the photogenerated electron and hole or reaction intermediates. Therefore, these negatively influence to the photocatalytic activity and performance. The results in Table 1 clearly suggest that the addition of metal ion, particularly the ions belonging to the first group, is effective for improving the photocatalytic performance of Ga_2O_3 to the overall splitting of H_2O. Among the ions in the first group, the addition of Zn ion is most effective for improving the photocatalytic activity. Therefore, the detailed examination was carried out on Zn ion modified Ga_2O_3.

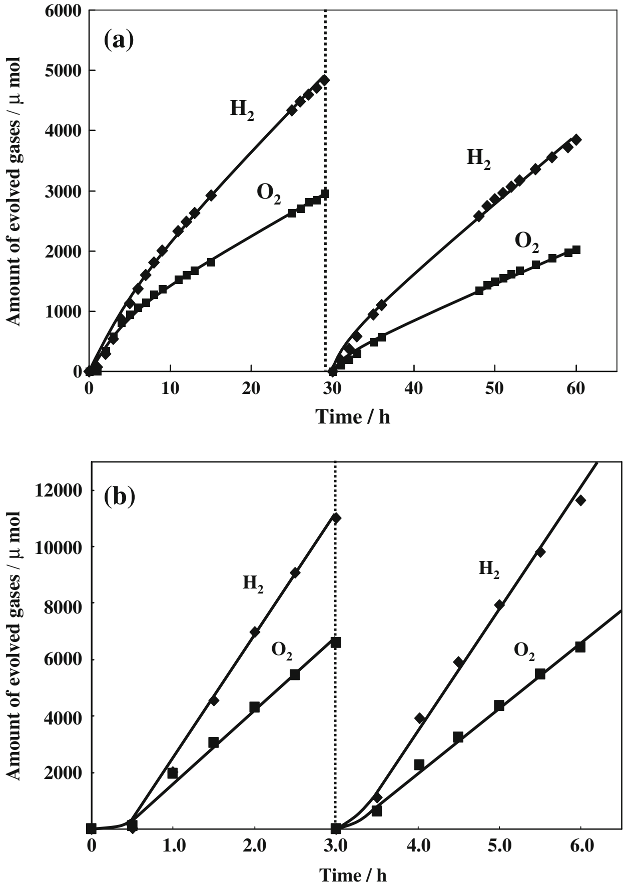

Fig. 1 Evolution of H_2 and O_2 in time over (**a**) Ni(1 wt%)/Ga_2O_3 and (**b**) Ni(1 wt%)/Zn(1 atm%)-Ga_2O_3, where Zn ion added Ga_2O_3 was prepared at 1,273 K

Figure 2 shows the dependence of the photocatalytic activity of Zn ion added Ga_2O_3 as a function of the amount of Zn ion added. The photocatalytic activity improved with

Table 1 Photocatalytic activity of Ni(1 wt%)/Ga_2O_3 modified with various metal ions

Metal ion*	Activity/μ mol	
	H_2	O_2
None	338	171
Ca	950	550
Sr	640	282
Ba	765	348
Cr	707	385
Ta	534	256
Zn	2,403	1,400
Mg	289	125
Ni	156	68
La	232	146
Ti	15	61
Fe	0.4	0
Co	4	4
Cu	14	27
Nb	2	33
Rh	12	0

* The amounts of added metal ions were 2 atomic % to Ga ion in the photocatalysts

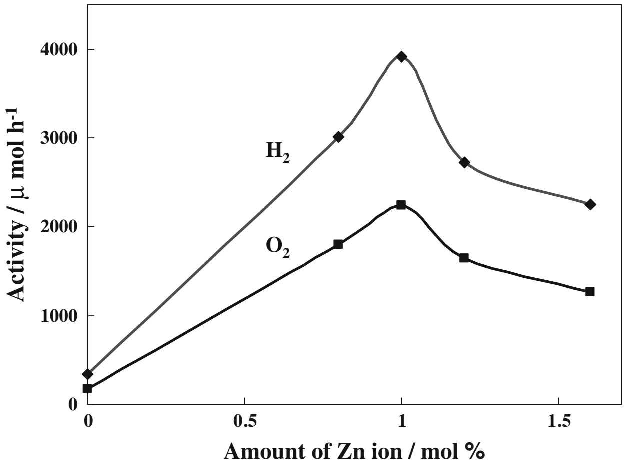

Fig. 2 Dependence of photocatalytic activity of Ni(1 wt%)/Zn-Ga_2O_3 to H_2O splitting as a function of the amount of added Zn ion

increasing amount of Zn ion, with the Ga_2O_3 photocatalyst that contains 1 atomic % of Zn ion shows the maximum activity, after which the activity decreases monotonously on further addition of Zn.

Figure 3 shows the effects of the preparation temperature of Zn (1 atom %)-Ga_2O_3 on the photocatalytic activity of H_2O splitting. The photocatalytic activities of H_2 and O_2 production improve with increasing the preparation temperatures and the photocatalyst prepared at around 1,223 K is preferable for photocatalytic splitting of H_2O, while the activity decreased with increasing the preparation temperature above 1,273 K. These results clearly shows that the addition of relatively small amount of Zn ion to Ga_2O_3 is effective and relatively high calcination temperature is necessary for preparing Zn ion added Ga_2O_3 with high photocatalytic performance in H_2O splitting. The preferable state of Zn added Ga_2O_3 photocatalyst contains 1 atomic % of Zn ion and obtained by calcining at around 1,223 K. The photocatalytic activity of H_2O splitting over Ni(1 wt%)/Zn(1 atom %)—Ga_2O_3 is 4,100 μmol/h for H_2 and 2,200 μmol/h for O_2 production, respectively. In order to evaluate the photocatalytic activity, the photocatalytic activity of NiO supported Tantalate photocatalysts, which carried out nearly the same photo-reaction system, were investigated from previous reports [1, 2, 14–16]. It was confirmed that the photocatalytic activity of Ni/Zn-Ga_2O_3 exhibited the same extent as alkali or alkali earth tantalum mixed oxide photocatalysts. Kato et al. [16] reported the apparent quantum yield of a NiO/$NaTaO_3$, which exhibited nearly the same photocatalytic activity on H_2O splitting as Ni/Zn-Ga_2O_3 under the same reaction condition. The apparent quantum yield of photocatalytic H_2O splitting over NiO/$NaTaO_3$ was 20%. These suggest that the apparent quantum yield of Ni/Zn-Ga_2O_3 probably shows around 20%.

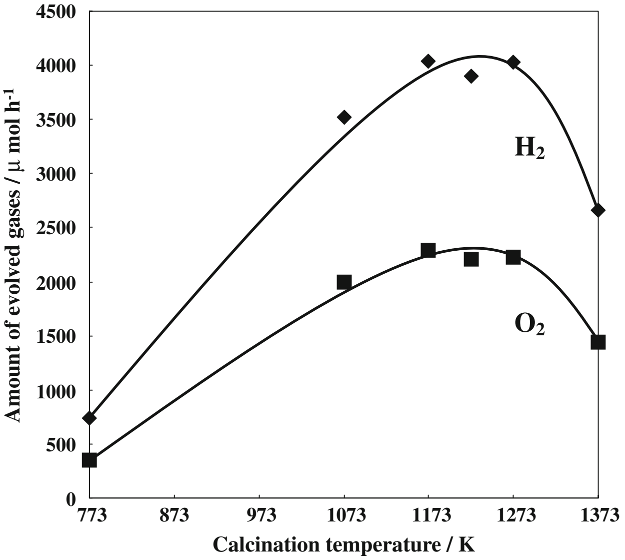

Fig. 3 Dependence of photocatalytic activity of Ni(1 wt%)/Zn(1 atmoic%)-Ga_2O_3 to H_2O splitting as a function of preparation temperature

In order to know the state of the Zn added Ga_2O_3 photocatalyst, the changes in the property and the structure of Ga_2O_3 photocatalyst due to the modification by Zn ions were examined.

From the results of UV diffuse reflectance spectrum, it was confirmed that the spectrum of Zn (1 atom %)-Ga_2O_3 was good agreement with that of Ga_2O_3 itself. This result suggests that no influence gave to the band gap excitation by the addition of Zn ion. From the spectrum, absorption edge attributable to band gap excitation appeared at 275 nm and the band gap was estimated to be 4.5 eV from the absorption edge.

The XRD patterns of Ga_2O_3 and Zn ion containing Ga_2O_3 are shown in Fig. 4, where Fig. 4a shows the XRD patterns in wide angle range. The XRD pattern of Ga_2O_3, which is the starting material of Zn ion added Ga_2O_3, is shown in Fig. 4(a-1). The pattern in Fig. 4(a-1) is good agreement with that of β-Ga_2O_3. Fig. 4(a-2, -4) shows the XRD patterns of Ga_2O_3 modified with various amount of Zn ion in the present work. These Zn ion modified Ga_2O_3 photocatalysts were prepared at 1,273 K. As shown in Fig. 4(a-2, -4), the main diffraction patterns are substantially the same as that of Fig. 4(a-1). However, the generation of a new diffraction peak at 36 degree can be confirmed in the patterns of Ga_2O_3 added with Zn ion more than 2 atomic % as shown in Figs. 4(a-3, -4). This peak is attributable to the main diffraction peak of $ZnGa_2O_4$. These results mean that the crystal structure of β-Ga_2O_3 is substantially the same after the addition of Zn ions in Ga_2O_3 and the generation of $ZnGa_2O_4$ phase can be confirmed by the addition of Zn ion more than 2 atomic %. Further detailed examination was carried out.

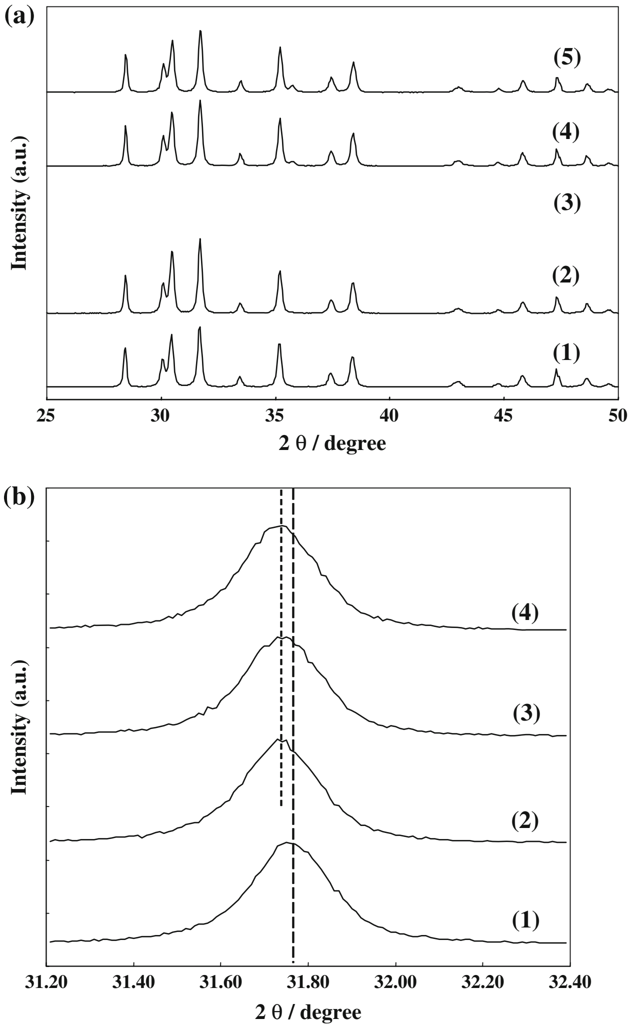

Fig. 4 XRD pattern of Ga_2O_3 added with various amount of Zn ion: (**a**) XRD patterns in wide range; the amounts of Zn ion in Ga_2O_3 are (1) 0, (2) 0.5, (3) 1, (4) 2 and (5) 3 atomic %, and (**b**) the diffraction peak of (−2 0 2) reflection; the amounts of Zn ion in Ga_2O_3 are (1) 0, (2) 1, (3) 2, and (3) 3 atomic %

Figure 4b shows the X-ray diffraction peak of (−2 0 2) reflection of Ga_2O_3 contained with various amount of Zn ion. The diffraction peak systematically shifts to lower angle with increasing the amount of added Zn ion up to 2 atomic %, while the peak position does not change significantly by the addition of Zn ion more than 2 atomic %, where the main peak of $ZnGa_2O_4$ phase is also present in the diffraction pattern as shown in Fig. 4(a-3, -4). When a metal ion becomes a dopant and replaces an original lattice ion, the XRD peaks systematically shift to lower or higher angle with increasing the amount of added metal ion as a function of the ion radius. The peak is shifted to lower angle if the ionic radius of added metal ion is larger than that of metal ion in the substrate, while the peak shifted higher angle if the ion radius is smaller. In this case, the ion radius of Ga^{3+} is 0.060 nm, while that of Zn^{2+} is 0.069 nm. As a result, the XRD pattern of Ga_2O_3 shifts to lower angle when Zn ions act as dopants in Ga_2O_3. The results in Fig. 4 clearly show that the added Zn ion acts a dopant in the Ga_2O_3 lattice if Zn ion added up to 2 atomic %, while the formation of a $ZnGa_2O_4$ phase occurs if Zn ion added more than 2 atomic %. The influences of Zn ion addition to the morphology of Ga_2O_3 were examined by FE-SEM.

From the results of the FE-SEM examination, no clear changes were observed in the morphologies of Ga_2O_3 before and after the doping of Zn ion.

These results suggest that the improvement of the photocatalytic performance to H_2O splitting has its origin in the qualitative change of the Ga_2O_3 by doping with Zn ion. Various effects of the doping of Zn on the Ga_2O_3 photocatalyst can be postulated that could improve the photocatalytic performance. The formation of $ZnGa_2O_4$ phase is one of the possibilities. However, the amount of $ZnGa_2O_4$ is very small and this mixed oxide did not exhibit high photocatalytic activity on the H_2O splitting [4]. Arai, et al. [17] reported that divalent metal ions, such as Mg^{2+} and Zn^{2+}, doped GaN combined with RuO_2 as co-catalyst become a stable photocatalyst for overall H_2O splitting. In this case, accepter level was formed in the forbidden band of GaN by doping of the divalent ions. The generation of photocatalytic activity on H_2O splitting was associated with increase in the mobility and concentration of holes due to the formation of the accepter level. The same effect of the addition of divalent ions to a GaN photocatalyst is one of the candidates for improving the photocatalytic activity of metal ion doped Ga_2O_3 photocatalysts.

However, in the results in Table 1, addition of divalent ion to Ga_2O_3 does not always improve the photocatalytic activity. Therefore, it is difficult to clearly identify the underlying reasons. Further detailed examinations are performed in order to elucidate the effects of metal ions addition, in particular Zn ion doping, to the remarkable improvement of photocatalytic activity on H_2O splitting.

It is concluded that Ga_2O_3 is one of the promising photocatalyst for over all splitting of H_2O and the photocatalyst can easily improve its performance by the addition of small amount of metal ion. Among the metal ions, Ca, Sr, Ba, Cr, Ta, and Zn ions were effective for improving the photocatalytic performance to overall splitting of H_2O. Particularly, the addition of Zn ion gives a remarkable effect to improve the photocatalytic activity. The preferable state of Zn added Ga_2O_3 was prepared by the calcination of Ga_2O_3 contained with 1 atomic % of Zn ion at 1,223 K.

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